



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

0663411 A1

1449

⑫ EUROPEAN PATENT APPLICATION

② Application number: 95100522.2

⑤ Int. Cl. #: C08F 299/02, G03F 7/038

22 Date of filing: 17.01.95

③ Priority: 17.01.94 JP 3248/94

④ Date of publication of application:  
19.07.95 Bulletin 95/29

④ Designated Contracting States:  
CH DE FR GB I L SE

(7) **Applicant: Nippon Kayaku Kabushiki Kaisha**  
11-2, Fujimi-cho 1 chome  
Chiyoda-ku  
Tokyo (JP)  
**Applicant: Nippon Polytech Corp.**  
358-2, Nibukata-cho  
Hachioji-shi,  
Tokyo (JP)

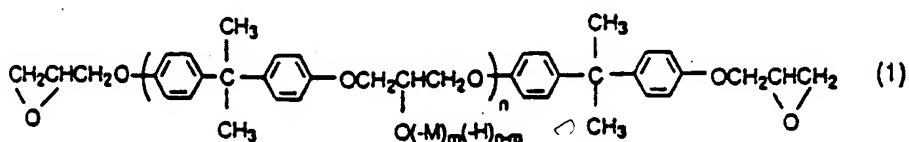
② Inventor: Yokoshima, Minoru  
2291 Ino  
Toride-shi,  
Ibaraki-ken (JP)  
Inventor: Ohkubo, Tetsuo

Nakano-Kaisaku,  
Konan-ku  
Ube-shi,  
Yamaguchi-ken (JP)  
Inventor: Sasahara, Kazunori  
11-15-401 Chofu-Innai-cho  
Shimonoseki-shi,  
Yamaguchi-ken (JP)  
Inventor: Sato, Yoneji  
1646 Kawaguchi-cho  
Hachioji-shi,  
Tokyo (JP)  
Inventor: Baba, Yoko  
22-23 Aburadaira Aza Agino  
Akigawa-shi,  
Tokyo (JP)

76 Representative: Türk, Gille, Hrabal, Leifert  
Brucknerstrasse 20  
D-40593 Düsseldorf (DE)

54 Photo-imaging resist ink and cured product thereof.

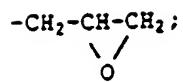
57 There is disclosed a photo-imaging resist ink containing (A) an unsaturated group-having polycarboxylic acid resin which is a reaction product of (c) succinic anhydride with an additive reaction product of (a) an epoxy resin with (b) an unsaturated group-having monocarboxylic acid, wherein (a) the epoxy resin is represented by the following formula (1):



wherein M stands for

EP 0 663 411 A1

Missing  
Pages  
6-9



n is at least 1  
on the average; and m is 1 to n on the average.

In forming a solder resist pattern by exposing a coating film of a resist ink through a patterned film to ultraviolet light and developing the coating film to dissolve away the unexposed portions thereof, the foregoing resist ink is excellent in developability and photosensitivity, while the cure product thereof is excellent in flex resistance and folding resistance, and well satisfactory in adhesion, pencil hardness, solvent resistance, acid resistance, heat resistance, etc. Accordingly, the resist ink is especially suitable as a liquid solder resist ink for flexible printed circuit boards and thin pliable rigid circuit boards.

BACKGROUND OF THE INVENTIONFIELD OF THE INVENTION

5 The present invention relates to a photo-imaging resist ink and a cured product thereof. More particularly, the present invention relates to a photo-imaging resist ink usable for a solder resist, a plating resist, etc. and developable with a dilute alkaline aqueous solution in the course of production of a flexible printed circuit board and a thin pliable rigid circuit board, and a cured product thereof excellent in flex resistance, folding resistance, adhesion, chemical resistance, heat resistance, etc.

10 DESCRIPTION OF THE PRIOR ART

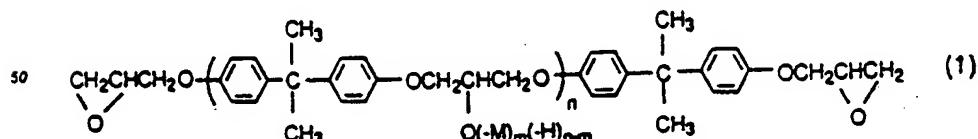
15 Ultraviolet-curing compositions have recently been increasingly used in various fields for reasons of resources saving, energy saving, improved workability, improved productivity, etc. For the same reasons, ultraviolet-curing compositions have begun to be used, instead of conventional thermosetting compositions, for various inks such as a solder resist ink and a marking ink in the field of manufacture of printed circuit boards. For example, Japanese Patent Publication No. 40,329/1981 discloses a curable photosensitive material comprising a reaction product of an epoxy resin-photopolymerizable  $\alpha,\beta$ -unsaturated carboxylic acid adduct with a dibasic carboxylic acid anhydride, a photopolymerizable monomer and a 20 photopolymerization initiator. Solder resists, which have heretofore been used in polyimide substrates called flexible printed circuit boards, are of a type wherein a polyimide film called a cover lay film is cut with a cutting die produced according to a pattern and then adhered to a substrate with an adhesive, or of a type wherein a flexibility-imparted ultraviolet-curing or thermosetting solder resist ink is applied on a substrate according to screen printing. Solder resists used in general printed circuit boards called rigid circuit boards 25 have also been increasingly required to have a high accuracy and a high resolution in order to materialize a higher packaging density in keeping with the advance of electronics. Since accuracy of a pattern cannot be secured according to conventional screen printing, a liquid photoresist method was proposed, which is now adopted at a rate of at least 50%.

30 A higher packaging density has recently been required in the field of flexible printed circuit boards as well. Some conventional liquid solder photoresists, though capable of securing accuracy of a pattern, are rigid in the form of a coating film and poor in adhesion to polyimides to fail to secure sufficient flexibility and folding resistance though they can secure an accuracy of a pattern, while the other conventional liquid solder photoresists, though flexible to a certain degree, are poor in workability and insufficient in chemical resistance and heat resistance. Thus, they involve problems in any case.

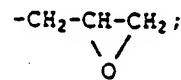
35 SUMMARY OF THE INVENTION

40 As a result of intensive investigations with a view to solving the foregoing problems, the inventors of the present invention have found out that a resist ink developable with a dilute alkaline aqueous solution and capable of forming a cured coating film excellent in flexibility, folding resistance, adhesion, chemical resistance, heat resistance, etc. can be prepared by using a specific polycarboxylic acid resin.

45 More specifically, the present invention provides:  
 (1) a photo-imaging resist ink containing (A) an unsaturated group-having polycarboxylic acid resin which is a reaction product of (c) succinic anhydride with an additive reaction product of (a) an epoxy resin with (b) an unsaturated group-having monocarboxylic acid, wherein (a) the epoxy resin is represented by the following formula (1):



55 wherein M stands for



$n$  is at least 1

on the average; and  $m$  is 1 to  $n$  on the average.

(2) a photo-imaging resist ink as set forth in (1) above, wherein  $n$  is 1 to 10 on the average;

(3) a photo-imaging resist ink as set forth in (1) above, wherein it is 1 to 10 on the average, polycarboxylic acid resin is prepared by reacting (a) the epoxy resin with 0.8 to 1.3 mol, per equivalent of the epoxy groups of (a) the epoxy resin, of (b) the unsaturated group-having monocarboxylic acid to form the additive reaction product, and subsequently reacting the above-mentioned additive reaction product with 0.1 to 0.9 equivalent, per equivalent of the hydroxyl groups of the additive reaction product, of (c) succinic anhydride;

(4) a photo-imaging resist ink as set forth in (1) or (3) above, wherein the acid value of (A) the unsaturated group-having polycarboxylic acid resin is 40 to 110 mg.-KOH/g.;

(5) a photo-imaging resist ink as set forth in (1) above, wherein the amount of (A) the unsaturated group-having polycarboxylic acid resin is 10 to 80 wt.% based on the total amount of the resist ink;

(6) a photo-imaging resist ink as set forth in (1) above, wherein (b) the unsaturated group-having monocarboxylic acid is a member selected from the group consisting of acrylic acid, acrylic acid dimer, methacrylic acid,  $\beta$ -styrylacrylic acid,  $\beta$ -furfurylacrylic acid, crotonic acid,  $\alpha$ -cyanocinnamic acid, cinnamic acid, half esters as reaction products of a saturated or unsaturated dibasic acid anhydride with a (meth)acrylate derivative having one hydroxyl group per molecule, half esters as reaction products of a saturated or unsaturated dibasic acid with an unsaturated group-having monoglycidyl compound, and mixtures thereof;

(7) a photo-imaging resist ink as set forth in (1) above, wherein (b) the unsaturated group-having monocarboxylic acid is acrylic acid;

(8) a photo-imaging resist ink comprising (A) an unsaturated group-having polycarboxylic acid resin set forth in (1) above, (B) a photopolymerization initiator, (C) a diluent, and (D) a curing component;

(9) a photo-imaging resist ink as set forth in (1) or (8) above, which is a solder resist ink;

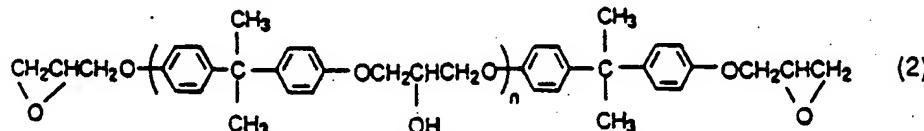
(10) a cured product of a photo-imaging resist ink as set forth in (1) or (8) above; and  
(11) a process for curing a photo-imaging resist ink comprising reacting a

(11) a process for curing a photo-imaging resist ink, comprising coating a substrate with a photo-imaging resist ink as set forth in (1) or (8) above, and subsequently irradiating the coated surface of the substrate with ultraviolet light.

The unsaturated group-having polycarboxylic acid resin (A) to be used in the present invention can be prepared by reacting the epoxy resin (a) of the above-mentioned formula (1) with the unsaturated group-having monocarboxylic acid (b) to synthesize an additive reaction product (I), and subsequently reacting the product (I) with succinic anhydride. Specifically, in the first reaction, hydroxyl groups are formed through an addition reaction of the epoxy residues of the epoxy resin (a) with the carboxyl residues of the monocarboxylic acid (b). In the second reaction, the polycarboxylic acid resin (A) is formed through an esterification reaction of the above-mentioned hydroxyl groups with succinic anhydride.

In the epoxy resin (a) of the aforementioned formula (1), n is at least 1 on the average, preferably 1 to 10 on the average, further preferably 3 to 5 on the average; and m is 1 to n on the average, preferably 1 to 0.8n on the average. The epoxy equivalent of the epoxy resin (a) is desirably about 200 to about 600.

45 preferably about 250 to about 500, further preferably about 270 to about 450. The epoxy resin (a) can be prepared by reacting the alcoholic hydroxyl group(s) of a compound represented by the following formula (2):



wherein n is at least 1 on the average, with an epihalohydrin such as epichlorohydrin preferably in the presence of dimethyl sulfoxide. The amount of the epihalohydrin to be used may be at least 1 equivalent per equivalent of the alcoholic hydroxyl group(s) of the compound of the formula (2). When it exceeds 15

equivalents per equivalent of the alcoholic hydroxyl group(s) of the compound of the formula (2), however, the effect of increasing it is observed substantially no more, while the volumetric efficiency is deteriorated.

The amount of dimethyl sulfoxide, if used, is preferably 5 wt.% to 300 wt.% based on the compound of the formula (2). When it is smaller than 5 wt.% based on the compound of the formula (2), the reaction of the alcoholic hydroxyl group(s) of the compound of the formula (2) with the epihalohydrin is slowed down to require a longer reaction time. On the other hand, when it exceeds 300 wt.% based on the compound of the formula (2), the effect of increasing it is observed substantially no more, while the volumetric efficiency is deteriorated.

An alkali is used in effecting the reaction. An alkali metal hydroxide is preferred as the alkali. Usable examples of the alkali metal hydroxide include caustic soda, caustic potash, and lithium hydroxide, among which caustic soda is preferable. Alternatively, calcium hydroxide may be used. The amount of the alkali to be used may be around 1 equivalent per equivalent of the alcoholic hydroxyl group(s) to be epoxidized of the compound of the formula (2). When all of the alcoholic hydroxyl group(s) of the compound of the formula (2) is epoxidized, an excessive amount of the alkali may be used. When it exceeds 2 equivalents per equivalent of the alcoholic hydroxyl group(s) of the compound of the formula (2), however, a little polymerization tends to occur.

The alkali metal hydroxide may be used either in a solid form or in the form of an aqueous solution thereof. When it is used in the form of an aqueous solution thereof, the reaction may be effected under ordinary or reduced pressure while distilling water off from the reaction system. The reaction temperature is preferably 30 to 100°C. When the reaction temperature is lower than 30°C, the reaction is slowed down to require a prolonged reaction time. When the reaction temperature exceeds 100°C, a side reaction unfavorably occurs to a great extent.

The residues of the epihalohydrin and dimethyl sulfoxide may be distilled off under reduced pressure after the completion of the reaction, and the formed resin may then be dissolved in an organic solvent and subjected to a dehydrohalogenation reaction with the alkali metal hydroxide. Alternatively, the reaction mixture may be washed with water after the completion of the reaction to separate therefrom a by-product salt and dimethyl sulfoxide, the excess of the epihalohydrin may be distilled off from the remaining oil layer under reduced pressure, and the formed resin may then be dissolved in an organic solvent and subjected to a dehydrohalogenation reaction with the alkali metal hydroxide. Usable examples of the organic solvent to dehydrohalogenation reaction with the alkali metal hydroxide. Usable examples of the organic solvent to include methyl isobutyl ketone, benzene, toluene, and xylene, among which methyl isobutyl ketone is preferred. Additionally stated, these organic solvents may be used either alone or in mixture. The epoxy resin (a) prepared according to the foregoing method is preferably such that 1 to n, preferably 1 to 0.8n, of the number n of the hydroxyl group(s) of the compound of the formula (2) are epoxidized. Additionally stated, the compound of the formula (2) is commercially sold, for example, under the name of Epikote 1001, 1002, 1003, 1004, etc. by Yuka Shell Epoxy K.K.

The aforementioned unsaturated group-having monocarboxylic acid (b) will now be described. Specific examples of the monocarboxylic acid (b) include acrylic acid, acrylic acid dimer, methacrylic acid,  $\beta$ -styrylacrylic acid,  $\beta$ -furfurylacrylic acid, crotonic acid,  $\alpha$ -cyanocinnamic acid, cinnamic acid, and the following half esters (1) and (2). These monocarboxylic acids (b) may be used either alone or in mixture. An especially preferred monocarboxylic acid is acrylic acid.

(1) An equimolar reaction product of a saturated or unsaturated dibasic acid anhydride with a (meth)acrylate derivative having one hydroxyl group per molecule.  
 (2) An equimolar reaction product of a saturated or unsaturated dibasic acid with an unsaturated group-having monoglycidyl compound.

Examples of the saturated or unsaturated dibasic acid anhydrides in (1) above include succinic anhydride, maleic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, methyltetrahydrophthalic anhydride, itaconic anhydride, and methylendomethylenetetrahydrophthalic anhydride. Examples of the (meth)acrylate derivative having one hydroxyl group per molecule in (1) above include hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, glycerol di(meth)acrylate, trimethylolpropane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, and (meth)acrylate of phenyl glycidyl ether.

Examples of the saturated or unsaturated dibasic acid in (2) above include succinic acid, maleic acid, adipic acid, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, itaconic acid, and fumaric acid. On the other hand, examples of the unsaturated group-having monoglycidyl compound in (2) above include glycidyl (meth)acrylate.

Synthesis Example 2

Substantially the same procedure as in Synthesis Example 1 except that the amount of 98.5% NaOH used was 24.3 g was repeated to effect a reaction to thereby obtain 365 g of an epoxy resin (a-2) having an epoxy equivalent of 379, a hydrolyzable chlorine content of 0.067%, a softening point of 76.8°C, and a melt viscosity (at 150°C) of 11.0 P. The epoxy resin (a-2) thus obtained was such that about 1.7 of 3.3 alcoholic hydroxyl groups in the epoxy resin of the formula (2) were epoxidized when calculated from the epoxy equivalents of the two epoxy resins.

10 Synthesis Example 3

Substantially the same procedure as in Synthesis Example 1 except that the amount of 98.5% NaOH used was 13.3 g was repeated to effect a reaction to thereby obtain 350 g of an epoxy resin (a-3) having an epoxy equivalent of 444, a hydrolyzable chlorine content of 0.054%, a softening point of 79.5°C, and a melt viscosity (at 150°C) of 11.5 P. The epoxy resin (a-3) thus obtained was such that about 1.0 of 3.3 alcoholic hydroxyl groups in the epoxy resin of the formula (2) was epoxidized when calculated from the epoxy equivalents of the two epoxy resins.

Synthesis Examples of Unsaturated Group-Having Polycarboxylic Acid Resin (A)20 Synthesis Example 4

2,870 parts (10 equivalents) of the epoxy resin (a-1) obtained in Synthesis Example 1, 720 parts (10 equivalents) of acrylic acid, 2.8 parts of methylhydroquinone, and 1943.5 parts of Carbitol acetate were charged, heated at 90°C, and stirred to effect dissolution of the reaction mixture. Subsequently, the liquid reaction mixture was cooled to 60°C, charged with 16.8 parts of triphenylphosphine, and then heated at 100°C to effect a reaction for about 32 hours to thereby obtain a reaction product having an acid value of 1.0 mg-KOH/g. Subsequently, the reaction product was charged with 783 parts (7.83 mol) of succinic anhydride and 421.8 parts of Carbitol acetate, and heated at 95°C to effect a reaction for about 6 hours. The reaction mixture was cooled to obtain a solution of an unsaturated group-having polycarboxylic acid resin (A-1) having an acid value (as solid) of 100 mg-KOH/g, a solid content of 65%, and a viscosity (at 25°C) of 250 P.

Synthesis Example 5

35 3,650 parts (10 equivalents) of the epoxy resin (a-2) obtained in Synthesis Example 2, 720 parts (10 equivalents) of acrylic acid, 3.4 parts of methylhydroquinone, and 2,366 parts of Carbitol acetate were charged, heated at 90°C, and stirred to effect dissolution of the reaction mixture. Subsequently, the liquid reaction mixture was cooled, charged with 20.1 parts of triphenylphosphine, and then heated at 100°C to effect a reaction for about 32 hours to thereby obtain a reaction product having an acid value of 1.0 mg-KOH/g. Subsequently, the reaction product was charged with 953 parts (9.5 mol) of succinic anhydride and 513 parts of Carbitol acetate, and heated at 95°C to effect a reaction for about 6 hours. The reaction mixture was cooled to obtain a solution of an unsaturated group-having polycarboxylic acid resin (A-2) having an acid value (as solid) of 100 mg-KOH/g, a solid content of 65%, and a viscosity (at 25°C) of 450 P.

Synthesis Example 6

4,440 parts (10 equivalents) of the epoxy resin (a-3) obtained in Synthesis Example 3,720 parts (10 equivalents) of acrylic acid, 4.0 parts of methylhydroquinone, and 2,794 parts of Carbitol acetate were heated at 90°C, and stirred to effect dissolution of the reaction mixture. Subsequently, the liquid reaction mixture was cooled, charged with 25.5 parts of triphenylphosphine, and then heated at 100°C to effect a reaction for about 32 hours to thereby obtain a reaction product having an acid value of 1.0 mg-KOH/g. Subsequently, the reaction product was charged with 1,125 parts of succinic anhydride and 608 parts of Carbitol acetate, and heated at 95°C to effect a reaction for about 6 hours. The reaction mixture was cooled to obtain a solution of an unsaturated group-having polycarboxylic acid resin (A-3) having an acid value (as solid) of 100 mg-KOH/g, a solid content of 65%, and a viscosity (at 25°C) of 620 P.

Examples 1 to 3 and Comparative Examples 1 and 2

According to a formulation (numerical values are parts by weight) as shown in Table 1, all components were milled with a triple roll mill to prepare a photo-imaging resist ink. The whole surface of a copper-clad polyimide film substrate (copper thickness: 12  $\mu\text{m}$ , polyimide film thickness: 25  $\mu\text{m}$ ) formed into a pattern was coated with the photo-imaging resist ink by screen printing while using a 100-mesh polyester screen to form a coating film having a thickness of 20 to 30  $\mu\text{m}$ , which was then dried in a hot-air dryer at 80°C for 30 minutes. Subsequently, a negative film having a resist pattern was brought into close contact with the dried coating film, which was then irradiated with ultraviolet light (quantity of exposure: 500  $\text{mJ/cm}^2$ ) while using an ultraviolet exposure apparatus Model HMW-680GW manufactured by Oak Co., Ltd. Subsequently, the coating film was developed with a 1% aqueous solution of sodium carbonate at a spray pressure of 2.0  $\text{kg/cm}^2$  for 60 seconds to dissolve away the unexposed portions thereof. The resulting product was evaluated with respect to developability and photosensitivity as will be described below. Thereafter, the product was heated and cured in the hot-air dryer at 150°C for 40 minutes to obtain a test piece having a cured coating film. This test piece was tested with respect to adhesion, pencil hardness, solvent resistance, acid resistance, heat resistance, flex resistance, and folding resistance as will be described below. The results are shown in Table 1. The test methods and the evaluation methods are as follows.

## (Developability)

20 The following ratings of evaluation were employed.

- The ink could be perfectly removed and developed by development thereof.
- △ A slight residue of the ink remained when it was developed.
- ✗ An undeveloped portions of the ink remained when it was developed.

## (Photosensitivity)

30 A step tablet with 21 steps (manufactured by Stauffer Chemical Co.) was brought into close contact with the dried coating film, which was then irradiated with, or exposed to, ultraviolet light (integrated quantity of light: 500  $\text{mJ/cm}^2$ ). Subsequently, the coating film was developed with a 1% aqueous solution of sodium carbonate at a spray pressure of 2.0  $\text{kg/cm}^2$  for 60 seconds to confirm the number of step for the remaining undeveloped coating film. The following ratings of evaluation were employed.

- at least step 9.
- △ step 6 to 8.
- ✗ at most step 5.

## (Adhesion)

40 In accordance with JIS K5400, 1-mm cross-cuts of 100 of the coating film were formed on the test piece, and then subjected to a peeling test with a Cellotape. The peeled state of the cross-cuts was observed, and evaluated according to the following ratings.

- not peeled with 100/100.
- △ 50/100 to 90/100.
- ✗ 0/100 to 50/100.

## (Pencil Hardness)

It was evaluated according to JIS K5400.

## (Solvent Resistance)

The test piece was immersed in isopropyl alcohol at room temperature for 30 minutes. After confirmation of whether or not something abnormal occurred in the appearance of the coating film, the test piece was subjected to a peeling test with a Cellotape, and evaluated according to the following ratings.

55 ○ Nothing abnormal occurred in the appearance of the coating film without blistering and peeling.

✗ The coating film was blistered and peeled.

(Acid Resistance)

5 The test piece was immersed in a 10% aqueous solution of hydrochloric acid at room temperature for 30 minutes. After confirmation of whether or not something abnormal occurred in the appearance of the coating film, the test piece was subjected to a peeling test with a Cellotape, and evaluated according to the following ratings.

- o Nothing abnormal occurred in the appearance of the coating film without blistering and peeling.
- X The coating film was blistered and peeled.

10 (Heat Resistance)

15 The test piece was coated with a rosin flux, and then immersed in a solder bath at 260°C for 5 seconds. The foregoing procedure as one cycle was repeated three times (three cycles). The test piece was allowed to cool to room temperature, then subjected to a peeling test with a Cellotape, and evaluated according to the following ratings.

- o Nothing abnormal occurred in the appearance of the coating film without blistering and peeling.
- X The coating film was blistered and peeled.

(Flex Resistance)

20 It was evaluated according to JIS K5400. The test piece was used with a stem of 2 mm in diameter to observe whether or not the coating film was cracked.

(Folding Resistance)

25 It was evaluated according to JIS C5016. The curvature radius of the folded surface was set to be 0.38 mm. The number of times of folding was counted until the coating film was cracked.

30

35

40

45

50

55

Table 1

	Ex.			Comp. Ex.	
	1	2	3	1	2
5 Unsaturated Group- having Poly- carboxylic Acid Resin (A-1) Obtained in Synthesis Example 4	69				
10 Unsaturated Group- having Poly- carboxylic Acid Resin (A-2) Obtained in Synthesis Example 5		54			
15 Unsaturated Group- having Poly- carboxylic Acid Resin (A-3) Obtained in Synthesis Example 6			54		
20 KAYARAO ZBR- *1				59	
KAYARAD PCR- *2					54
U-200AX *3		5.0	5.0		5.0
M-325 *4		3.5	3.5		3.5
KAYARAD DPHA *5	3.5			3.5	
IRGACURE 907 *6	3.0	3.0	3.0	3.0	3.0
KAYACURE DETX-S *7	0.5	0.5	0.5	0.5	0.5
KAYACURE 9MS *8	1.0	1.0	1.0	1.0	1.0
R-1415-1 *9	10.0				
EXA-4800 *10		10.0	10.0	10.0	10.0
30 Dicyandiamide (epoxy- curing agent)	0.5	0.5	0.5	0.5	0.5
Silica (inorganic filler)	10.0	10.0	10.0	10.0	10.0
Phthalocyanine Green (pigment)	0.5	0.5	0.5	0.5	0.5
35 Aerosil #200 *11	1.0	1.0	1.0	1.0	1.0
MODAFLOW *12	1.0	1.0	1.0	1.0	1.0
Developability	o	o	o	o	o
Photosensitivity	o	o	o	o	o
40 Adhesion	o	o	o	o	o
Pencil Hardness	4H	5H	5H	4H	7H
Flex Resistance	not cracked	not cracked	not cracked	not cracked	cracked
Folding Resistance	at least 1,000 times	at least 1,000 times	at least 1,000 times	at least 1,000 times	once
45 Solvent Resistance	o	o	o	o	o
Acid Resistance	o	o	o	o	o
Heat Resistance	o	o	o	o	o

## Note)

\*1) KAYARAD ZBR-: manufactured by Nippon Kayaku Co., Ltd., a reaction product of bisphenol A epoxy acrylate (manufactured by Yuka Shell Epoxy K.K., a reaction product of EPIKOTE 1004 with acrylic acid) with succinic anhydride, containing 24.5 wt.% of Carbitol acetate and 10.5 wt.% of solvent naphtha and having an acid value (as solid) of 100 mg·KOH/g.

\*2) KAYARAD PCR-: manufactured by Nippon Kayaku Co., Ltd., a reaction product of phenolic novolak epoxy acrylate (manufactured by Nippon Kayaku Co., Ltd., a reaction product of EPPN-201 with acrylic acid) with succinic anhydride, containing 24.5 wt.% of Carbitol acetate and 10.5 wt.% of solvent naphtha and having an acid value (as solid) of 100 mg·KOH/g.

\*3) U-200AX: manufactured by Shin-Nakamura Chemical Co., Ltd., a urethane acrylate.

\*4) M-325: manufactured by Toagosei Chemical Industry Co., Ltd., caprolactone-modified tris(acryloxyethyl) isocyanurate.

\*5) KAYARAD DPHA: manufactured by Nippon Kayaku Co., Ltd., a mixture of dipentaerythritol penta- and hexa-acrylates.

\*6) IRGACURE 907: manufactured by CIBA-GEIGY Ltd., a photopolymerization initiator, 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propanone.

\*7) KAYACURE DETX-S: manufactured by Nippon Kayaku Co.,

Ltd., a photopolymerization initiator, 2,4-diethylthioxanthone.

- \*8) KAYACURE BMS: manufactured by Nippon Kayaku Co., Ltd., a photopolymerization initiator, 4-benzoyl-4'-methylphenyl sulfide.
- \*9) R-1415-1: manufactured by A.C.R. Co., Ltd., a rubber-modified epoxy resin.
- \*10) EXA-4800: manufactured by Dainippon Ink & Chemicals, Inc., a bisphenol S epoxy resin.
- \*11) Aerosil #200: manufactured by Nippon Aerosil Co., Ltd., anhydrous silica.
- \*12) MODAFLOW: manufactured by Monsanto Co., a leveling agent.

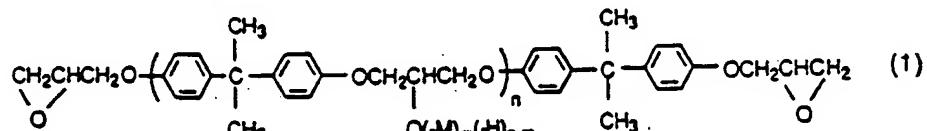
As is apparent from the results of evaluation as shown in Table 1, the resist inks according to the present invention were excellent in developability and photosensitivity, and the cure products thereof according to the present invention were excellent in flex resistance, folding resistance, solvent resistance, acid resistance, heat resistance, etc.

## EFFECT OF THE INVENTION

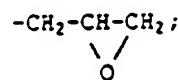
35 In forming a solder resist pattern by exposing a coating film of a photo-imaging resist ink through a patterned film to ultraviolet light and developing the coating film to dissolve away the unexposed portions thereof, the photo-imaging resist ink of the present invention is excellent in developability and photosensitivity, while the cure product thereof is excellent in flex resistance and folding resistance, and well satisfactory in adhesion, pencil hardness, solvent resistance, acid resistance, heat resistance, etc. Accordingly,  
40 the resist ink of the present invention is especially suitable as a liquid solder resist ink for flexible printed circuit boards and thin pliable rigid circuit boards.

## Claims

45 1. A photo-imaging resist ink containing (A) an unsaturated group-having polycarboxylic acid resin which is a reaction product of (c) succinic anhydride with an additive reaction product of (a) an epoxy resin with (b) an unsaturated group-having monocarboxylic acid, wherein (a) said epoxy resin is represented by the following formula (1):



wherein  $M$  stands for



5

$n$  is at least 1  
on the average; and  $m$  is 1 to  $n$  on the average.

10 2. A photo-imaging resist ink as claimed in claim 1, wherein n is 1 to 10 on the average.

15 3. A photo-imaging resist ink as claimed in claim 1, wherein (A) said unsaturated group-having polycarboxylic acid resin is prepared by reacting (a) said epoxy resin with 0.8 to 1.3 mol, per equivalent of the epoxy groups of (a) said epoxy resin, of (b) said unsaturated group-having monocarboxylic acid to form said additive reaction product, and subsequently reacting said additive reaction product with 0.1 to 0.9 equivalent, per equivalent of the hydroxyl groups of said additive reaction product, of (c) succinic anhydride.

20 4. A photo-imaging resist ink as claimed in claim 1 or 3, wherein the acid value of (A) said unsaturated group-having polycarboxylic acid resin is 40 to 110 mg·KOH/g.

25 5. A photo-imaging resist ink as claimed in claim 1, wherein the amount of (A) said unsaturated group-having polycarboxylic acid resin is 10 to 80 wt.% based on the total amount of the resist ink.

30 6. A photo-imaging resist ink as claimed in claim 1, wherein (b) said unsaturated group-having monocarboxylic acid is a member selected from the group consisting of acrylic acid, acrylic acid dimer, methacrylic acid,  $\beta$ -styrylacrylic acid,  $\beta$ -furfurylacrylic acid, crotonic acid,  $\alpha$ -cyanocinnamic acid, cinnamic acid, half esters as reaction products of a saturated or unsaturated dibasic acid anhydride with a (meth)acrylate derivative having one hydroxyl group per molecule, half esters as reaction products of a saturated or unsaturated dibasic acid with an unsaturated group-having monoglycidyl compound, and mixtures thereof.

35 7. A photo-imaging resist ink as claimed in claim 1, wherein (b) said unsaturated group-having monocarboxylic acid is acrylic acid.

40 8. A photo-imaging resist ink comprising (A) an unsaturated group-having polycarboxylic acid resin as claimed in claim 1, (B) a photopolymerization initiator, (C) a diluent, and (D) a curing component.

45 9. A photo-imaging resist ink as claimed in claim 1 or 8, which is a solder resist ink.

50 10. A cure product of a photo-imaging resist ink as claimed in claim 1 or 8.

55 11. A process for curing a photo-imaging resist ink, comprising coating a substrate with a photo-imaging resist ink as claimed in claim 1 or 8, and subsequently irradiating the coated surface of said substrate with ultraviolet light.

45

50

59



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 95 10 0522

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
A,D	US-A-3 980 483 (T. NISHIKUBO ET AL.) 14 September 1976 " example 13 "	1-11	C08F299/02 G03F7/038
A	EP-A-0 362 735 (NIPPON KAYAKU K.K.) 11 April 1990 " page 3, line 20 - line 43 " " page 4, line 31 "	1-11	
A	DE-A-27 05 612 (DAINIPPON INK AND CHEMICALS) 11 August 1977 " page 13, paragraph 2 " " page 16, paragraph 2 "	1-11	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	20 April 1995	J.-M. DUPART	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons R : member of the same patent family, corresponding documents			